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Electrical properties of sol-gel derived barium titanate ceramics

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Abstract : The electrical (ferroelectric, dielectric, piezoelectric and pyroelectric) properties of sol-gel processed barium titanate ($BaTiO_3$) ceramics have been reported. The room temperature dielectric constant (ε) and loss tangent (tan δ) were found to be 1235 and 0.012 respectively. Both ε and tan δ showed anomaly peaks at 125°C. The piezoelectric charge coefficient (d_{33}) and effective electromechanical coupling coefficient (k_{eff}) were respectively found to be 187×10^{-12} C–N^{-1} and 0.20 respectively The pyroelectric coefficient (P_i) of the ceramics was found to be 3×10^{-9} C–cm^2–K^{-1} and shows anomaly peak at 125°C confirming the ferroelectric to paraelectric phase transition

Keywords : Phase transition, electrical properties, sol-gel derived $BaTiO_3$ ceramics

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1. Introduction

There has been considerable interest in ferroelectric ceramics due to possible applications in piezoelectric [1], pyroelectric [2], electro-optic [3], acousto-optic [4] and memory [5] devices. Barium titanate is a perovskite ferroelectric material with many useful properties [6]. Extensive studies have been made on the properties of $BaTiO_3$ ceramics prepared by solid state reaction method [7–10]. Recently, the sol-gel technique have been utilised for the fabrication of $BaTiO_3$ powder [11] and ceramics [12]. The advantages of the sol-gel technique are easy composition control, low processing temperature, fine particle size and short fabrication cycle. A little studies has been made on the electrical properties of the sol-gel processed barium titanate ceramics. In this paper, we report the electrical (ferroelectric, dielectric, piezoelectric and pyroelectric) properties of sol-gel derived $BaTiO_3$ ceramics.

2. Experimental

Barium titanate ceramics were prepared from barium acetate [$Ba(CH_3COO)_2$] and titanium (IV) isopropoxide [$Ti((CH_3)_2CHO)_4$] precursors. Barium acetate was first dissolved in acetic acid [CH_3COOH] and an equimolar amount of $Ti((CH_3)_2CHO)_4$ was then added dropwise, keeping it constantly stirred. The solution was finally diluted with methoxy ethanol [$CH_3(CH_2)_2OH$] and filtered using a micro glass fibre filter paper. The filtrate was set aside (for about 24 hour) till a white opaque gel was obtained. The gel was converted to white powder after firing at 350°C for one hour in air. The powder was then annealed at 700°C for one hour in air for crystallization. Ceramic samples were prepared by pressing the powder in the form of circular discs, using a pressure of 1.25×10^3 kg cm^{-2}, and sintering at 1300°C for two hours in air.

The structural and microstructural characterizations of the ceramics were carried out by using a Philips (PW 1840) X-ray diffractometer and a Jeol (JSM 840) scanning electron microscope respectively. The polarization-field (*P–E*) characteristics was measured at 50 Hz by using a modified Sawyer-Tower circuit. The longitudinal piezoelectric charge coefficient (d_{33}) was measured by using a Berlincourt's d_{33} meter. The piezoelectric coupling coefficient or electromechanical coupling coefficient (k) was measured from the resonant and antiresonant frequencies with the help of HP 4194A impedance analyser. The dielectric properties were investigated by using a HP 4192A capacitance bridge. The pyroelectric properties were studied by measuring the pyroelectric current at different temperatures. The above measurements were carried out on the samples in the metal-ferroelectric-metal (MFM) configuration. The samples were prepared by electroding the sintered ceramic discs (1 cm diameter and 0.1 cm thick) with silver paste and poling in oil at 150°C using a poling field of 30 KV cm^{-1}.

3. Results and discussions

3.1. Structure and microstructure :

The as-fired powder was found to be amorphous which crystallized to tetragonal $BaTiO_3$ after annealing at 700°C for one hour in air (Figure 1). The lattice parameters a and c were

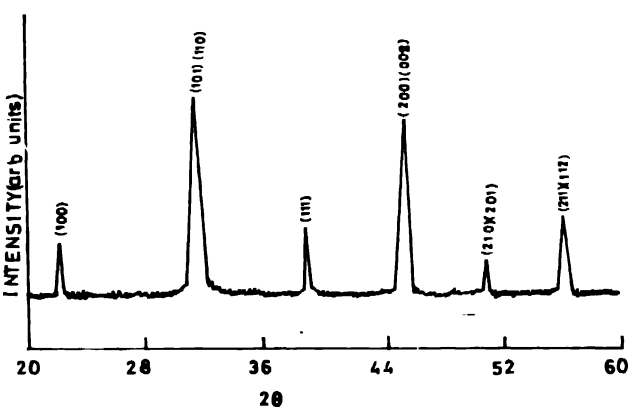

Figure 1. X-ray diffraction pattern of sol-gel processed $BaTiO_3$ ceramics sintered at 1300°C for two hours in air.

Plate I

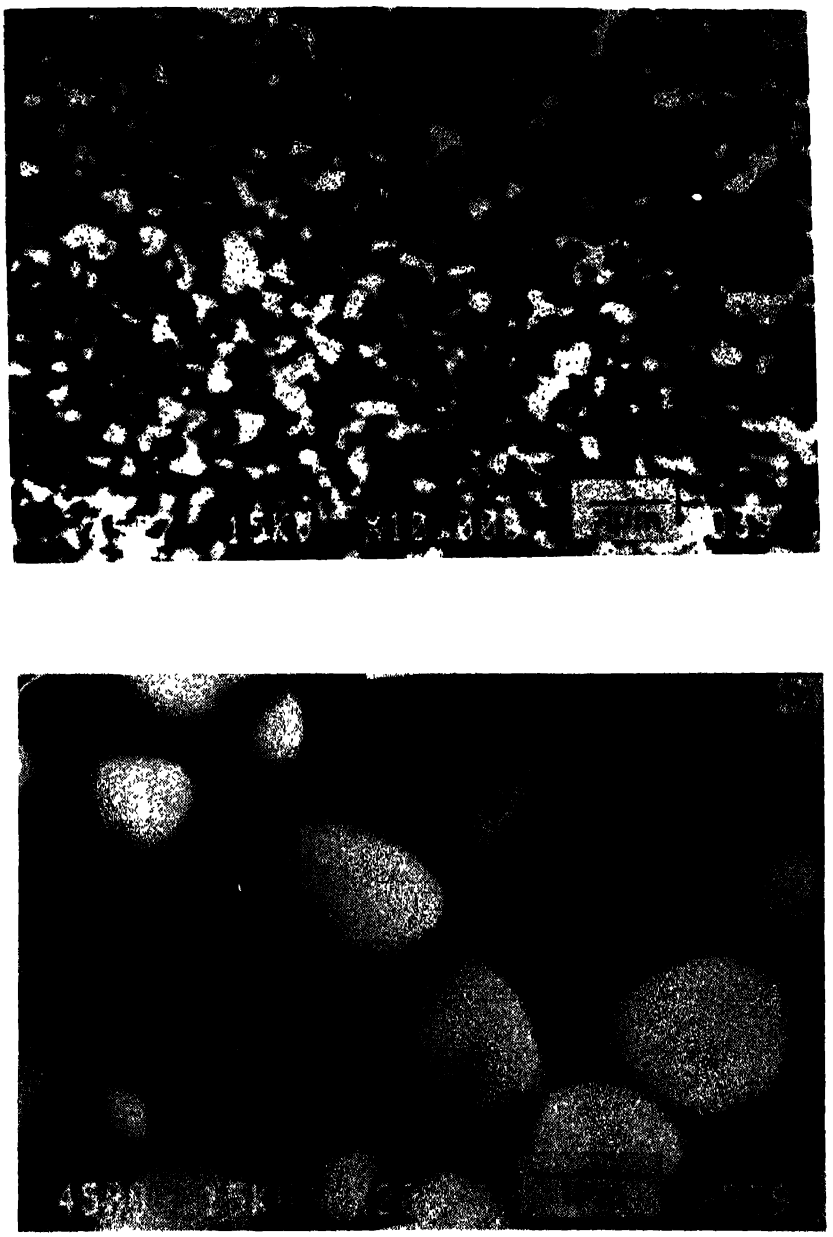

Figure 2. Scanning electron micrographs of (a) unsintered and (b) sintered $BaTiO_3$ ceramics.

Plate II

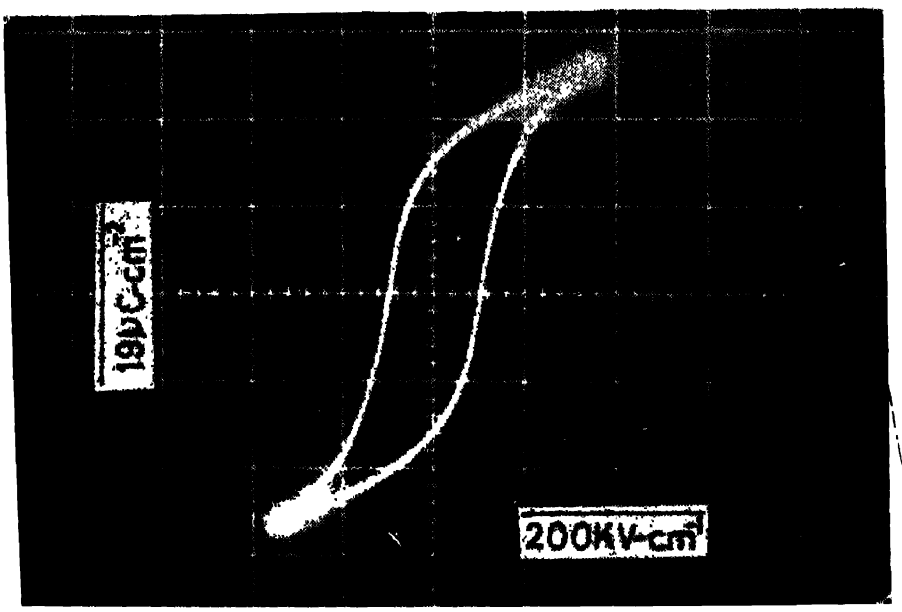

Figure 3. Polarization-Field (P–E) hysteresis loop of $BaTiO_3$ ceramic.

found to be 3.994 and 4.035 Å. The unsintered ceramics have small particles (< 1 μm) (Figure 2(a)) which coalesced to form larger well defined grains after sintereing at 1300°C for two hour in air (Figure 2(b)).

3.2. *Ferroelectric properties :*

The polarization-field hysteresis measurements of the ceramics were carried out to check the ferroelectricity in the samples. The room temperature P–E hystereris loop shows well saturation (Figure 3). The values of the remanent polarization, spontaneous polarization and coercive field was found to be 12.6, 19.0 μC-cm^{-2} and 30 KV cm^{-1} respectively. The polarization values is slightly lower than that of $BaTiO_3$ single crystal [13], whereas the coercive field is higher. The lower values of the polarization and higher values of the coercive field of ferroelectric ceramics as compared to their single crystal counterparts have been well documented in the literature [14–16]. This has been attributed to the existence of the space charged layers of the metal-ferroelectric interface and grain boundaries [17].

3.3 *Dielectric properties* :

The dielectric constant (ε) and loss tangent (tan δ) at 1 KHz of the ceramics were found to be 1235 and 0.012 respectively. The dielectric constant showed a slight frequency dispersion in the frequency range 100 Hz–1 MHz (Figure 4). The value of ε of the ceramics

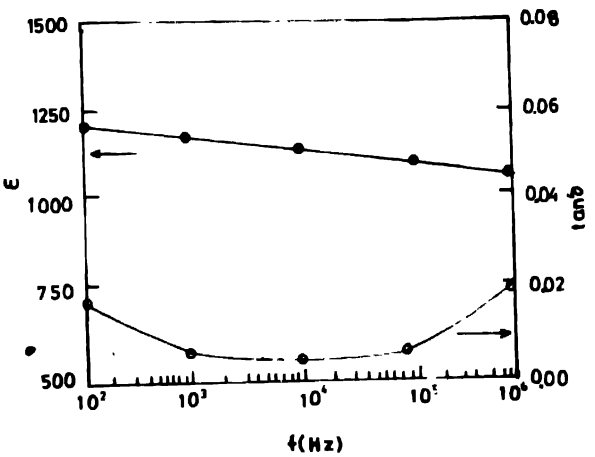

Figure 4. Variation of dielectric constant (ε) and loss tangent (tan δ) of $BaTiO_3$ ceramic with frequency

is lower than that reported for $BaTiO_3$ single crystal [18]. Figure 5 shows the variation of ε and tan δ at 1 KHz with temperature. It may be noted that both ε and tan δ showed anomaly peaks at 125°C, confirming the ferroelectric-paraelectric phase transition. The peak is broad and lower in magnitude as compared to that of $BaTiO_3$ single crystal [18]. Similar results have been reported for ferroelectric ceramics [6]. The lowering in the dielectric constant

and broadening of the dielectric anomaly peak in the ceramics may be attributed to (i) lower density and smaller grain size or (ii) existence of the space charged layers at the electrode-ferroelectric interface and grain boundaries [17]. More studies on the dielectric properties of the ceramics having different grain sizes are needed for better understanding of the observed experimental results.

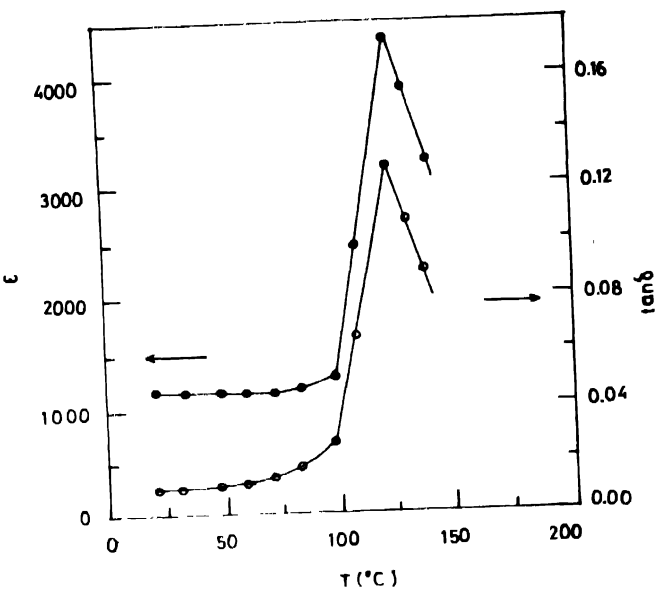

Figure 5. Variation of dielectric constant (ε) and loss tangent (tan δ) of $BaTiO_3$ ceramic with temperature

3.4. Piezoelectric properties :

When a piezoelectric ceramic is subjected to an alternating electric field, then the mechanical deformations (expansion and contraction) become large when the frequency of the applied signal approaches the mechanical resonance frequency of the ceramic. The piezoelectric coupling coefficient or electromechanical coupling coefficient (k) can be determined from the resonant (f_r) and antiresonant (f_a) frequencies by identifying the mode of vibration for the system. For discs (used in the present measurements), the dominant mode of vibration depends on the ratio of the diameter (D) and the thickness (t') of the discs. For $D > 3.16\,t'$, the radial and the thickness modes of vibration dominates. The longitudinal and transverse electromechanical coupling coefficients (k_{33} and k_{31} respectively) are given by :

$$k_{33}^2 = \pi/2/(1+\Delta f/f_r)^{-1}\tan\left[\frac{\pi}{2}\Delta f/f_r/(1+\Delta f/f_r)\right], \quad (1)$$

$$k_{31}^2 \quad \pi/2[1+\Delta f/f_r]\tan\left(\frac{\pi}{2}\Delta f/f_r\right), \quad (2)$$

where $\Delta f = f_a - f_r$. The effective coupling coefficient (k_{eff}) of an arbitrary resonator at the fundamental overtone or at any overtone can be expressed as :

$$k_{eff}^2/(1-k_{eff}^2) = (f_a^2 - f_r^2)/f_r^2. \tag{3}$$

The planar coupling coefficient (k_p) can be calculated from the following relation :

$$k_p^2 = 2k_{31}^2/(1-\sigma^E) \tag{4}$$

where σ^E is the Poisson's ratio.

Figure 6 shows the variation of the impedance of the ceramic with the frequency. It may be noted that there was only one resonance in the frequency range 170–230 KHz. The resonance in the thickness mode is expected to occur at a higher frequency than that in the

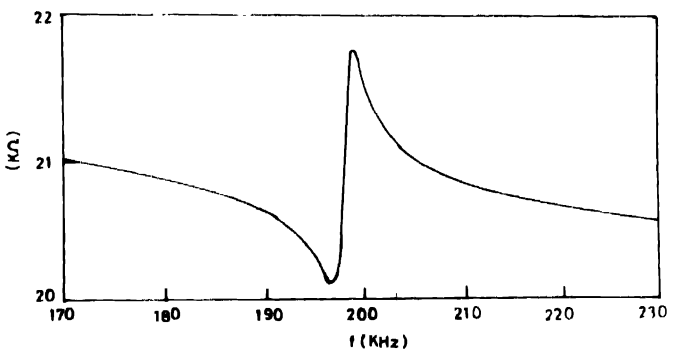

Figure 6. Variation of impedence (Z) of $BaTiO_3$ ceramics with frequency

radial mode. However, in the absence of the overtones and distinct resonance modes, it is difficult to identify the mode of vibration. Therefore, the K_{eff} was calculated using eq. (3) which was found to be 0.185. This value is close to k_{31} reported for $BaTiO_3$ single crystal and ceramics [19,20]. This suggests that the radial mode of vibration dominates and has been responsible for the resonance in the present measurements. The values of k_{31} and k_{33} calculated from eqs. (1) and (2) were found to be 0.20 and 0.22 respectively which are close to that reported for $BaTiO_3$ ceramics prepared by solid state reaction method [20]. An estimation of the transverse piezoelectric charge coefficient (d_{31}) can be evaluated from the relation :

$$d_{31} = k_{31}\sqrt{(\varepsilon_0 \varepsilon S_{11}^E)}, \tag{5}$$

where ε_0 is the free space permitivity (8.854×10^{-14} F–cm^{-1}) and $S_{11}{}^E$ is the elastic constant. The value of d_{31}, using $\varepsilon = 1235$ for the ceramic and $S_{11}{}^E = 8.55 \times 10^{-12}$ m^2–N^{-1} for $BaTiO_3$ single crystal, was found to be 59×10^{-12} C–N^{-1}. This value is close to the reported value for $BaTiO_3$ ceramics prepared by conventional mix oxide route [20]. The value of K_p calculated using eq. (4) was found to be 0.34 which is case to that reported for $BaTiO_3$ ceramics [20].

The measured value of d_{33} of the ceramic was found to be $187X^{-12}$ C–N^{-1} which is close to the reported values for $BaTiO_3$ ceramics prepared by thermochemical solid state reaction method [21]. The value of d_{33} drops to $5X^{-12}$ C–N^{-1} after depoling the sample by heating above the transition temperature (125°C). The original value was recovered by repoling the sample again. The value of d_{33} remained unchanged even after two years of poling.

3.5. Pyroelectric properties :

The pyroelectric properties of the ceramic were investigated by measuring the pyroelectric current at different temperatures for different intervals. Figure 7 shows the variation of temperature (T) and pyroelectric current (I_p) with heating time (t). The slope of

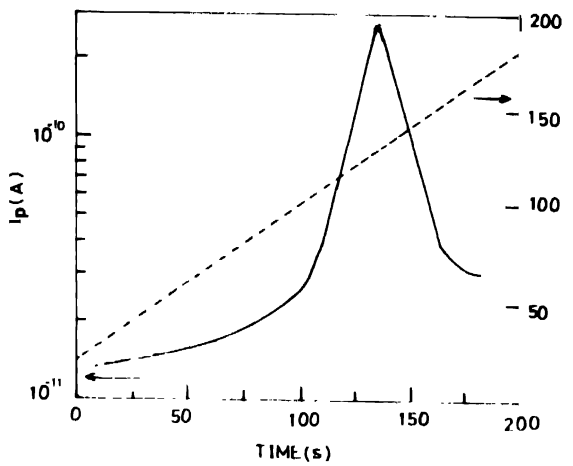

Figure 7. Variation of pyroelectric current (P_t) and temperature (T) with time (t) of $BaTiO_3$ ceramics

the temperature-time curve gives the rate of heating (dT/dt) and the pyroelectric coefficient was determined from :

$$P_t = I_p / A(dt/dT), \tag{6}$$

where Å is the area of the sample. Figure 8 shows the variation of P_t with temperature The value of P_t at the room temperature was found to be about 3×10^{-9} C–cm^{-2}–K^{-1} which is one order of magnitude lower than that of $BaTiO_3$ single crystal [16]. The lower value of P_t in ceramics may be due the random orientation of the crystallites as all of them may not be fully oriented along the polar axis even after poling. It may be noted from Figure 8 that the transition peak is broad and a measurable pyroelectric signal exists at the temperatures well above the transition temperature. The existence of the pyroelectric signal in the paraelectric phase in thin $BaTiO_3$ single crystal have been reported by earlier workers [22]. This has been attributed to polarised surface charged layer. The grain boundaries in ceramics may have different properties than the bulk due to the presence of the space charge fields. This electrical and mechanical strains may induce the different grains to

undergo the phase transition at different temperatures, thereby broadening and lowering the pyroelectric signal anomaly peak.

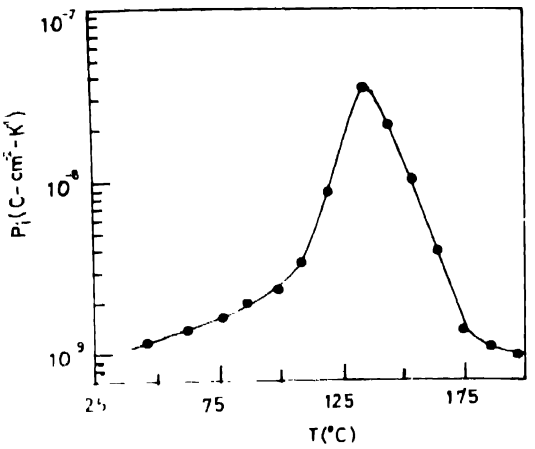

Figure 8. Variation of pyroelectric coefficient (P_i) of $BaTiO_3$ ceramics with temperature

4. Conclusion

The sol-gel processing technique can be used for the synthesis of good quality ferroelectric $BaTiO_3$ ceramics. The values of the spontaneous, remanent polarisations and coercive fields were found to be 19.0, 12.6 $\mu C-cm^{-2}$ and 30 $KV-cm^{-1}$ respectively. The room temperature dielectric constant and loss tangent were found to be 1235 and 0.012 respectively. Both ε and tan δ showed anomaly peaks at 125°C. The piezoelectric charge coefficients d_{33} and d_{31} were respectively found to be 187 and 59×10^{-12} $C-N^{-1}$ respectively. The values of the piezoelectric coupling coefficients k_{31}, k_{33} and k_p were found to be 0.20, 0.22 and 0.34 respectively. The values of the pyroelectric coefficient was found to be 3×10^{-9}–C–cm^{-2}–K^{-1}. The transition temperature determined from the pyroelectric and dielectric studies was found to be 125°C.

Acknowledgments

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